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Synthesis and characterization of alkali-metal aryloxo compounds and their catalytic activity for L-lactide polymerization

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ABSTRACT

Three new alkali-metal compounds stabilized by aryloxo groups were synthesized and fully characterized. The reactions of carbon-bridged bis(phenol)s $MBMPH_2$ ($MBMPH_2$ = 2,2′-methylene-bis(6-*tert*-butyl-4-methylphenol)) with sodium and potassium metals in tetrahydrofuran (THF) gave the desired alkali-metal complexes $[MBMPNa_2(THF)_3]_2$ (**1**) and $[(MBMPK_2)_2(THF)_5]_2$ (**2**), respectively, in high isolated yields. A similar reaction of aminophenol [HNOH] ([HNOH] = N-*p*-methyl-phenyl(2-hydroxy-3,5-di-*tert*-butyl)benzylamine) with sodium gave the monosodium salt $[HNONa(THF)]_2$ (**3**). Compounds **1**–**3** were well characterized, including X-ray structure determination. Compound **1** has a dimeric structure, and each sodium atom is four-coordinated with four oxygen atoms to form a distorted tetrahedron. Compound **2** has a centrosymmetric tetrameric structure. The coordination environments around the four potassium atoms are different. K1 is four-coordinated, K2 is three-coordinated, K3 is five-coordinated, whereas the coordination sphere of K4 is completed by one aryloxo oxygen atom and two oxygen atoms from two THF molecules and six carbon atoms from one arene ring of the bis(phenolate) ligand. Compound **3** has a dimeric structure, and each of the sodium atoms is four-coordinated to form a distorted tetrahedron. It was found that compounds **1**–**3** can efficiently initiate the ring opening polymerization of L-lactide in the absence of alcohol, yielding polymers with high molecular weights for a wide range of monomer-to-initiator ratios.

1. Introduction

In recent years, the synthesis of polylactide (PLA), as one kind of environment-friendly material, has received considerable attention because of its biorenewability, biodegradability and biocompatibility. Ring-opening polymerization (ROP) of lactide catalyzed by a metal catalyst is a convenient method for synthesizing polymers with high molecular weights and narrow molecular weight distributions [1]. Alkali-metal compounds are non-toxic and are easily available. Therefore, the application of alkali-metal compounds as the initiators for the polymerization of lactides has received attention for a considerable length of time. Alkali-metal compounds such as butyllithium, lithium *tert*-butoxide and potassium *tert*-butoxide have been used to initiate the polymerization of L-lactide or D,L-lactide, but the activities of these compounds are rather low and the molecular weight distributions of the polymers obtained are broad because of the presence of both chain termination and chain transfer side reactions [2]. In recent years, a series of novel alkali metal compounds stabilized by bridged bis(phenolate) groups were synthesized by Lin and his coworkers [3]. They have found that a proper steric barrier around the alkali-metal center and addition of an appropriate alcohol can minimize the intra- and inter molecular transesterification side reactions, and can polymerize the L-lactide in a controlled manner.

Herein we report the synthesis, characterization and catalytic behavior of three new alkali metal compounds stabilized by a carbon-bridged bis(phenolate) group $MBMP^{2-}$ [MBMP = CH_2(1-O-4-Me-6-Bu^t-C_6H_2)$_2$] and an aminophenolate group $[HNO]^-$ {[HNO] = *p*-Me-$C_6H_4NHCH_2$(2-O-3,5-Bu$^t_2$-C_6H_2)}. The experimental results demonstrate that these alkali metal compounds can initiate the ring-opening polymerization of L-lactide with high activity in the absence of alcohol, and the polymerization has a somewhat controlled character using sodium aminophenolate as the initiator.

2. Experimental

2.1. Materials and general procedures

All of the manipulations were performed under an argon atmosphere, using standard Schlenk techniques. Na, K and $MBMPH_2$ are commercially available. Tetrahydrofuran (THF) and toluene were dried and freed of oxygen by refluxing over sodium/benzophenone

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ketyl, and they were distilled prior to use, while isopropyl alcohol was first treated with CaH_2 powder for a few days to remove dissolved water and then distilled under vacuum. L-Lactide was recrystallized from toluene twice and stored in a dry box. [HNOH] was prepared according to the published procedure [4]. Carbon, hydrogen and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. The ^1H and ^{13}C NMR spectra were recorded in a $CDCl_3$ solution for compounds **1**–**3** with a Unity Varian 300 NMR spectrometer. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. The molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

2.2. Synthesis of $[MBMPNa_2(THF)_3]_2$ (**1**)

To a stirred THF suspension of Na (0.23 g, 10.00 mmol) was slowly added a THF solution of $MBMPH_2$ (1.36 g, 4.00 mmol) at −20 °C. The mixture was stirred for 6 h at room temperature, and then THF was evaporated to about 20 mL under reduced pressure. Colorless crystals were obtained after several days (1.99 g, 76%). Mp: 139–140 °C. *Anal.* Calcd. for $C_{70}H_{108}Na_4O_{10}$: C, 69.97; H, 9.06. Found: C, 69.89; H, 8.95%. ^1H NMR (300 MHz, $CDCl_3$): 7.04–6.44 (m, 8H, ArH), 3.90–3.40 (m, 28H, α-CH_2 THF + CH_2), 2.33–2.00 (m, 12H, CH_3), 1.76 (s, 24H, β-CH_2 THF), 1.40–0.99 (m, 36H, Bu^t). $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): 156.34, 153.00, 144.62, 142.38, 142.02, 138.88, 136.28, 134.67, 131.32, 129.23, 128.67, 128.36, 128.33, 128.13, 127.77, 127.03, 126.74, 126.55, 126.00, 125.22, 124.46, 77.58, 77.362, 76.74, 68.09, 47.56, 47.1, 35.77, 35.19, 35.11, 35.01, 34.91, 34.86, 34.76, 34.71, 34.60, 34.26, 31.52, 31.49, 31.35, 31.20, 31.06, 30.88, 30.60, 30.51, 30.41, 30.18, 29.89, 29.74, 29.67, 29.44, 29.21, 25.65, 21.23, 21.17, 21.08, 21.00, 20.87, 20.71. IR (KBr, cm^{-1}): 2951(s), 2905(s), 2866(s), 1656(m), 1645(m), 1474(m), 1443(s), 1416(m), 1361(m), 1052(m), 880(m), 823(m), 505(s).

2.3. Synthesis of $[(MBMPK_2)_2(THF)_5]_2$ (**2**)

The synthesis of compound **2** was carried out in the same way as that described for compound **1**, but K (0.39 g, 10.00 mmol) was used instead of Na. Colorless microcrystals were obtained from a concentrated THF solution (about 18 mL) in a few days (2.17 g, 86%). Mp: 200–201 °C. *Anal.* Calcd. for $C_{132}H_{200}K_8O_{18}$: C, 66.42; H, 8.44. Found: C, 66.57; H, 8.38%. ^1H NMR (300 MHz, $CDCl_3$): 7.12–6.00 (m, 16H, Ar), 3.68–3.09 (m, 48H, α-CH_2 THF + CH_2), 2.08–2.35 (m, 12H, CH_3), 1.78 (s, 40H, β-CH_2 THF), 1.40–1.03 (m, 84H, CH_3 + Bu^t). $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): 153.67, 151.08, 147.52, 144.89, 144.67, 143.62, 143.10, 142.10, 141.89, 141.80, 138.45, 138.26, 137.94, 137.55, 136.52, 134.35, 131.88, 129.82, 129.00, 128.81, 128.68, 128.62, 128.62, 128.49, 128.41, 128.07, 127.80, 127.25, 127.17, 127.02, 126.83, 126.64, 126.42, 126.26, 77.59, 77.36, 76.74, 68.12, 47.63, 47.11, 36.35, 35.19, 35.13, 34.99, 34.85, 34.79, 34.70, 34.46, 32.14, 31.50, 31.37, 31.21, 30.98, 30.55, 30.47, 30.42, 30.39, 30.21, 30.08, 29.83, 29.25, 29.13, 25.74, 23.31, 23.12, 22.07, 21.18, 20.98, 20.89. IR (KBr, cm^{-1}): 2955(s), 2905(s), 2866(s), 1628(m), 1605(m), 1543(m), 1474(s), 1416(m), 1362(m), 1046(m), 880(m), 833(m), 505(s).

2.4. Synthesis of $[HNONa(THF)]_2$ (**3**)

The synthesis of compound **3** was carried out in the same way as that described for compound **1**, but [HNOH] (1.30 g, 4.00 mmol), instead of $MBMPH_2$, and Na (0.23 g, 10.00 mmol) were used. The THF solution obtained was concentrated to 5 mL under reduced pressure, and then 15 mL toluene was added to the residue. Colorless crystals were obtained in several days (1.55 g, 79%). Mp: 239–241 °C. *Anal.* Calcd. for $C_{52}H_{76}N_2Na_2O_4$: C, 74.43; H, 9.13; N, 3.34. Found: C, 74.61; H, 8.91; N, 3.35%. ^1H NMR (300 MHz, $CDCl_3$): 7.75–7.55 (m, 4H, ArH), 7.50–7.25 (m, 4H, ArH), 6.75–6.50 (m, 4H, ArH), 4.24 (s, 4H, CH_2), 3.75–3.25 (br, s, 8H, α-CH_2 THF), 3.19 (s, 2H, NH), 2.27 (s, 6H, CH_3), 1.65 (s, 18H, Bu^t), 1.50 (s, 26H, β-CH_2 THF + Bu^t). $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): 147.76 (Ph), 146.77 (Ph), 129.96 (Ph), 128.94 (Ph), 128.38 (Ph), 127.74 (Ph), 123.68 (Ph), 115.97 (Ph), 67.85 (α-CH_2 THF), 50.80 (CH_2Ar), 35.56 ($C(CH_3)_3$), 34.14 ($C(CH_3)_3$), 32.51 ($C(CH_3)_3$), 30.48 ($C(CH_3)_3$), 25.80 (β-CH_2 THF), 20.66 (CH_3). IR (KBr, cm^{-1}): 3286(s), 2956(s), 2866(s), 1614(m), 1519(m), 1469(s), 1288 (s), 1236(m), 1055(s), 881(m), 818(s).

2.5. Procedure for the polymerization reaction

The procedures for the polymerization of L-lactide initiated by compounds **1**–**3** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask in a glovebox, equipped with a magnetic stirring bar, was charged with the desired amount of L-lactide, initiator and toluene. The mixture was stirred vigorously at 70 °C for the desired time, during which time an increase in the viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

2.6. X-ray crystallography

Suitable single crystals of compounds **1**–**3** were sealed in a thin-walled glass capillary for determination of the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. In complex **1**, seven THF molecules were found to be disordered over two sites with an occupancy factor of 0.50/0.50 for C47–C78/C47′–C78′. In the case of complex **2**, six THF molecules were found to be disordered over two sites with an occupancy factor of 0.50/0.50 for C47–C70/C47′–C70′ and O5–O10/O5′–O10′. Except the disordered atoms, all of the non-hydrogen atoms were refined anisotropically. The hydrogen atom on the N1 atom in complex **3** was located from the Fourier map. All other hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The structures were solved and refined using SHELXL-97 programs.

3. Results and discussion

3.1. Synthesis and characterization of compounds **1**–**3**

The carbon-bridged bis(phenol) $MBMPH_2$ reacts with excessive sodium in THF, after workup, to give the dimeric compound $[MBMPNa_2(THF)_3]_2$ (**1**) in a high isolated yield, as shown in Scheme 1. Compound **1** has been characterized by ^1H, ^{13}C NMR and IR spectroscopic studies, and elemental analysis. The ^1H NMR spectrum shows sets of resonances for the methyl and *tert*-butyl substituents on the phenyl rings at δ 2.03–2.33 and 1.07–1.40 ppm, respectively. Furthermore, one set of multiple resonances for the eight hydrogen atoms on the arene rings was observed at δ